Remarks/Arguments:

Claims 46-70, presented hereby, are pending.

Claims 20-27 and 29-45 are canceled, hereby, without prejudice or disclaimer.

Present claims 46-70 are the same as claims 20-27 and 29-45, respectively, amended pursuant to the CPA papers filed February 28, 2002. (Entry of the CPA amendment was incorrectly denied by the Office Action mailed December 3, 2003, as set forth in the paper filed April 2, 2004). [Originally presented by amendment filed December 31, 2001, the amendments were denied entry pursuant to the Advisory Action mailed 17 January 2002. For the examiner's convenience, the requisite marked-up version of the amended claims – claims 20 and 29 – submitted with the amendment filed December 31, 2001, is attached hereto as Appendix).

Claims were rejected under 35 USC 112, 1st ¶, for allegedly lacking enablement. Reconsideration is requested.

Rejected claims 20-45 were limited (by the amendment filed December 31, 2001) to the beverage subject matter "in the form of a submicron emulsion or micro-emulsion," i.e., the subject matter of claim 28, which subject matter was found enabled under 35 USC 112, 1st ¶, according to Office Action mailed July 23, 2001. Since present claims 46-70 are limited to the subject matter found allowable by the Examiner – the subject matter of claim 28 – the rejection is not applicable against the present claims.

Claims were rejected under 35 5 USC 112, 2nd ¶, for allegedly being indefinite, because the scope of each of the phrases "acceptable as an additive" and "visible solubility" was allegedly unknown. The rejection is inapplicable against the present claims.

Regarding the word "visible solubility", the present specification (page 5, lines 10 to 14) explains that such a solubility corresponds to an emulsion containing insoluble oil droplets that are invisible to the naked human eye. In other words, it means that the emulsion appearing to be a clear solution is, in reality, a true emulsion of insoluble droplets in an aqueous mixture. The emulsifier makes it possible to disperse essential oil in very fine droplets to the point where the droplets are invisible.

The phrase "acceptable as an additive in human food," in the rejected claims, was changed in the claims as amended December 31, 2001 – which change is reflected in the present claims – to read "acceptable for human consumption," as supported in the specification at page 3, lines 6-31.

The rejection of claims under 35 USC 103(a) based on US 4944956 (Brun), alone, is rendered moot by the amendment filed December 31, 2001. The amendment filed December 31, 2001, limited the rejected claims to the subject matter of claim 28, which was not rejected under §103(a) based on Brun, alone. The present claims being, also, limited to the subject matter of claim 28, are not subject to the rejection.

Reconsideration is requested with respect to the rejection under 35 USC 103(a) of the subject matter in claims 28 and 29 based on Brun in view of US 4966779 (Kirk).

First, the rewording effected by amending the rejected claims (in the amendment filed December 31, 2001, which is reflected in the present claims) overcomes the reasons for rejection set forth in item no. 11 of the final rejection (Office Action mailed December 2, 2003). The claims, as previously amended and as presented, hereby, clearly recite that the size of particles is limited to "an average diameter less than 100 namometers [0.1 μm]."

Secondly, the aforesaid added particle-size limitation renders the subject matter of the claims, as amended, patentable under §103(a), statements in the final rejection to the contrary notwithstanding, for the following reasons.

Brun teaches that clear ethanolic compositions become cloudy when they are diluted; but, the reference is silent on whether the emulsion is micronized and on the size of particles in the ethanolic compositions, as presently claimed. Kirk provides no teaching or suggestion to overcome these fatal deficiencies in Brun.

Kirk discloses an emulsion with an average droplet size of about 0.5 microns to about 8 microns, preferably from 0.5 micron to about 2 microns (Kirk column 4, line 32). In Example 2 (Kirk column 6, lines 5 and 6), the average emulsion droplet diameter is described as approximately 2 microns. The smallest droplet diameter described in Kirk is, thus, 0.5 micron, i.e., 500 nanometers. Moreover, at the droplet diameters described in Kirk, the reference, itself, teaches that the emulsion is not clear but, rather, appears as a milky emulsion (Kirk column 6, line 13).

On the contrary, the instant claimed invention is directed to a submicron emulsion (or micro-emulsion) composed of nanosomes, whose average diameter is *less than 100 nanometers*, which is

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five-fold smaller than the smallest droplet (i.e., 500 nanometers) in the Kirk emulsion. Thus, as

opposed to the *milky* Kirk emulsions, the presently claimed invention is a clear emulsion, i.e., an

emulsion with particle diameters so small it appears clear, as if it were a true *solution*.

The clarity of the beverage according to the presented claimed invention results from the fact

that it is in the form of a submicron emulsion (or micro-emulsion) composed of nanosomes, i.e.,

particles whose average diameter is less than 100 nanometers. Thus, the size of particles is so small

that the particles are imperceptible to the naked eye and, so, a clear phase liquid, comparable to a

true solution, but comprising an emulsion, is observed.

Moreover, the milky emulsions disclosed in Kirk are incorporated into a food product as

additives, such as for cereal fortification and other nutritional uses. On the other hand, the emulsions

according to the presently claimed invention are used for preparing non-alcoholic beverages, which

become cloudy when they are combined with water.

Attention is, further, directed to the method of preparing small nanosomes as found in the

presently claimed invention. As illustrated in the examples, the microemulsion is prepared by

mechanical treatment, which purpose is to reduce the droplet size in the emulsion and, thus, to

increase the clarity and the physical chemical stability of the emulsion (present specification, page

5, lines 32 to 37). This is done, e.g., using high pressure homogenization or high speed mixing or

using a Polytron (application page 11 – Example 5, line 16, and Example 6, line 26; page 12 –

Example 7, lines 11 and 12, and example 9, lines 31 and 32).

In connection with their response filed May 10, 2001, Applicants stressed that subjecting the emulsion disclosed in Kirk to high pressure treatment or high speed grinder mixing would cause the average particle diameter to be less than 100 nm; nonetheless, it would still not produce a clear solution, because the resulting emulsion would not be thermodynamically stable. Applicants submit that the chemical composition of the emulsion mixture is what allows for the apparent clarity of the emulsion and, so, the chemical composition of the emulsion disclosed in Kirk will always give milky emulsions.

Kirk teaches a composition of a water-miscible emulsion using specific proportions of (a) a fat-soluble vitamin, (b) a liquid edible vegetable oil, (c) a modified lecithin, (d) a sucrose ester, (e) a sorbitan monooleate, (f) a sugar alcohol and (g) water. The emulsion has an average droplet size of from about 0.5 micron to about 8 microns, preferably about 0.5 micron to about 2 microns, compounds (c), (d) and (e) being surfactants. On the contrary, the beverage according to the instant claimed invention comprises only one type of surfactant, i.e, one phospholipid.

The emulsion disclosed in Kirk is stable, i.e., it is an emulsion which does not separate into oil and water phases upon standing. Such an emulsion is not a clear solution, because the particles are perceptible to the naked eye, as explained above. Moreover, the Kirk emulsion is not intended to be diluted before consumption, no anethol is described as being present, and vitamins are completely different compounds with completely different uses.

For one skilled in the art and who wishes to provide clear beverages containing anethol, it would not have been obviousness to micronize the emulsion disclosed in Kirk in order to have

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smaller particles. The solubility threshold of anethol is greater for a given volume of alcohol, as disclosed in Figure 1 of the subject application, i.e., as shown by the graph in the figure.

Regarding the rejection as applied against claim 38 (present claim 63), the claim is directed to a cloudy beverage, which is obtained by diluting a clear beverage according to amended claim 20 (present claim 46). Indeed, the first object of the presently claimed invention is to provide a beverage that is clear before diluting (with water). The beverage is intended for consumption as diluted, and the dilution causing clouding. Examples of such a clear beverage, which become cloudy *only* upon diluting, include *Pastis* and other *aniseed-based* aperitif beverages of like kind (see present specification, page 1, lines 5 to 9, and page 2, lines 24 to 27).

Citation to, and reliance on, *In re Levin*, 84 USPQ 232 (CCPA 1949), in the statement of rejection is noted by Applicants. Reliance on *Levin* is, however, misplaced.

Under the rule set forth in *Levin*, the presently claimed invention, broadly (i.e., as defined in claim 28, claim 20 as amended, and present claim 46), is patentable. Moreover, the facts in *Levin*, which led to the holding of unpatentability in that case, are readily distinguishable from the facts in the present situation.

According to the decision in *Levin*:

> No single reference shows all of the ingredients and steps set forth in the appealed claims. However, more than one reference may be properly considered in determining the patentability of claims. Accordingly, *no point can be successfully made here that* in the combined references upon which the tribunals of the Patent Office relied *there was no clear disclosure or suggestion of each and every ingredient of the product . . .* defined by the appealed claims.

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84 USPQ at 233 (*emphasis added*). Thus, the holding of unpatentibility in *Levin* is expressly limited to fact situations in which "*no* point can be successfully made . . . that in the combined references . . . relied [upon] there was *no* clear disclosure or suggestion of each and every ingredient of the product."

In other words, the court in *Levin* held that the applicant/appellant could not contest the finding that "each and every ingredient" of the claims was disclosed "in the combined references upon which the . . . Patent Office relied." Contrary to the facts found in *Levin*, however, "each and every ingredient of the product" presently claimed is *not* found "in the combined references upon which the . . . Patent Office relied."

As opposed to the prior art relied on to reject the claims in *Levin*, the *combined teachings* of Brun and Kirk do *not* contain a "clear disclosure or suggestion" (84 USPQ at 233) of *anethol-phospholipid droplets* – i.e., "nanosomes having an average diameter less than 100 nanometers" – as recited in the present claims. Thus, the holding in *Levin* is not controlling under the *present* facts.

Of course the court in *Levin* did not find the claims unpatentable under 35 USC 103(a), since the decision antedated the changes in the patent laws occurring in 1952, which created Section 103. *Levin* is, however, consistent with post-1952 decisions holding that a finding of obviousness under Section 103 requires that all claim limitations must be found in the prior art in order to support a holding of obviousness, e.g., *In re Royka*, 180 USPQ 580 (CCPA 1974). "All words in a claim must be considered in judging the patentability of that claim against the prior art." *In re Wilson*, 165 USPQ 494, 496 (CCPA 1970). When conducting an obviousness analysis, "all limitations of a claim

must be considered in determining the claimed subject matter as is referred to in 35 USC 103 and it is error to ignore specific limitations distinguishing over the reference" relied on to reject the claims. *Ex parte Murphy*, 217 USPQ 479, 481 (PO Bd. App. 1982).

In the present situation, however, neither of the references relied on to reject the claims, taken alone or in combination, describes aqueous emulsions containing anethol-phospholipid droplets of less than 100 nanometers in diameter, i.e., "a submicron emulsion or micro-emulsion composed on nanosomes having an average diameter less than 100 nanometers of the type comprising anethol-phospholipid phase" (claim 28, claim 20 as amended, and present claim 46).

Accordingly, at least one limitation on rejected claim 28 (claim 20 as amended and present claim 46) is not supported by the prior art relied on to reject the claims under §103(a). Since "the cited references do not support each limitation of [the] claim," the rejection under §103(a) "is simply inadequate on its face." *In re Thrift*, 63 USPQ2d 2002, 2008 (Fed. Cir. 2002). Withdrawal of the rejection under 35 USC 103(a) appears to be in order.

Submitted herewith is the Declaration of Mr. Pascal Brunerie under 37 CFR 1.132 ("the Brunerie Declaration"), which, further, demonstrates patentability of the presently claimed invention under §103(a). Mr. Brunerie currently holds the position and title *Head of Chemistry* at Centre de Recherche Pernod Ricard (associated with assignee of record Pernod Ricard). On applicant's behalf, Mr. Brunerie analyzed the rejection under 35 USC 103(a) set forth in the final Office Action, and subsequent Advisory Action , in the subject application.

In Mr. Brunerie's expert opinion, the teachings of Kirk do not support the allegations set forth in the statement of rejection. That is, according to the statement of rejection (Office Action mailed February 14, 2001) (emphasis added):

> Brun et al . . . are silent as to whether the emulsion is micronized. Kirk teaches the production of [a] water miscible emulsion using a modified lecithin that is produced for the food industry in [a] size of 0.5 microns that is stable. It would have been obvious to those skilled in the art to *micronize* the emulsion of the prior art [Brun] in order to enhance the stabilization of the [Brun] food product.

In other words, the statement of rejection alleges that Kirk teaches a *microemulsion* by disclosing an emulsion having a 0.5 *micron* particle size.

The Brunerie Declaration confirms the aforesaid interpretation of Kirk, specifically that Krik neither teaches nor suggests a microemulsion.

In the words of Mr. Brunerie (Brunerie Declaration, ¶ bridging pages 1 & 2), contrary to the allegations contained on the statement of rejection,

> one skilled in the art would not have considered the particle size of at least 0.5 µm (500 nanometers) in the milky emulsion taught by Kirk to teach or suggest the particle size of at most 0.1 µm (100 nanometers) in the clear microemulsion in accordance with the invention described and claimed in the subject application.

> As detailed in the Brunerie Declaration, the word *microemulsion* is a term reserved – as known to one skilled in the art – for emulsions having a maximum droplet size of 0.1 µ (100 nanometers).

> The Brunerie Declaration relies on four, cited publications in explaining that the 0.5 µm-droplet-size emulsion of Kirk, neither teaches nor suggests a *microemulsion*. For example, as explained in the Brunerie Declaration (¶ bridging pages 1 and 2) (*emphasis in original*).

One skilled in the art would have typically reserved the term "microemulsion" to identify clear emulsions having droplet diameters no larger than 0.1 μm (100 nanometers) and to distinguish "emulsions," which are opaque (i.e., milky or cloudy) in appearance and have much larger droplet diameters. Moreover, one skilled in the art would have understood that this difference in droplet size is a determinative factor in the clarity/opacity difference. As set forth in *Microemulsion: A Definition*, online at URL http://surfactants.net/microemulsion.htm (copy attached, hereto):

> *Micro*emulsions are typically *clear solutions*, as the droplet diameter is approximately *100 nanometers or less*. . . . Emulsions (or *macro*emulsions) are in contrast unstable, the suspended droplets . . . are much larger, typically one micron or more, resulting in a *cloudy or milky* dispersion. [*Emphasis added.*]...

Kirk (US Pat. No. 4966779) does not disclose a *microemulsion*, either expressly or inherently. What Kirk does disclose are stable, water-miscible emulsions (i.e., *macro*emulsions) containing having a droplet particle size of 0.5-8 μm. Example 1 of Kirk describes such an emulsion as having a *milky aspect* (Kirk column 6, lines 12-13) and a droplet size of 2 μm (Kirk column 6, lines 5-6). The conspicuous absence from Kirk of any mention of the term *microemulsion* is consistent with the fact that milky emulsions having a particle size of 0.5 μm (or larger) would not have been considered *microemulsions* by one skilled in the art. On the contrary, the person skilled in the art would have considered Kirk's disclosure of particle sizes no less than 0.5 μm, being so far from the particle sizes (no larger than 100 nanometers) necessary for a microemulsion, as effectively *excluding* clear, microemulsions, i.e., as effectively *limited to* milky, non-microemulsions.
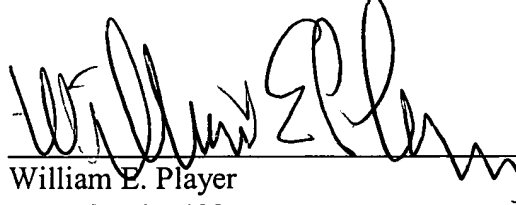
The Brunerie Declaration shows that Kirk, in effect, is deficient in the teachings necessary to have led one skilled in the art to change a *phospholipid-&-anethol-containing* **macro***emulsion beverage* to a *phospholipid-&-anethol-containing* **micro***emulsion beverage*, as in the subject matter presently claimed. When a reference in relied on in a rejection under §103(a) based on a combination of references, "individual defects of the reference . . . can defeat the rejection." *In re Lyons*, 150 USPQ 741, 746 (CCPA 1966).

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Favorable action is requested.

Respectfully submitted,

JACOBSON HOLMAN PLLC

By: _William E. Player_____
William E. Player
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Date: September 21, 2004
Attachment: Rule 132 Declaration of Pascale Brunerie
R:\Home\rthomas\2004\SEPTEMBER\P64053 amd&rule 132.wpd

APPENDIX

Marked-up Version of claims attached to amendment filed December 31, 2001

20   (amended). Alcoholic or nonalcoholic beverage containing anethol, comprising an effective amount of at least one phospholipid, acceptable [as an additive in human food, in order to improve the visible solubility of the anethol in said beverage] for human consumption, in the form of a submicron emulsion or micro-emulsion composed of nanosomes having an average diameter less than 100 nanometers, of the type comprising anethol-phospholipid phase in aqueous, alcoholic or non alcoholic phase.

29   (amended). Alcoholic or nonalcoholic beverage according to claim [28] 20, wherein the microemulsion is obtained by high-pressure homogenization or by an appropriate mixer at high speed.

Attorney Docket No. P64053US0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Brigitte FALCONNIER

Application No.: 09/423,665   Art Unit: 1761

Filed: November 22, 1999   Examiner: Curtis Edward SHERRER

For: NOVEL CLEAR BEVERAGE OPTIONALLY ALCOHOLIC CONTAINING
       ANETHOL AND CLOUDY DILUTED BEVERAGE OBTAINED BY DILUTION

DECLARATION UNDER 37 CFR 1.132

Mail Stop AF
Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

The undersigned, Pascal Brunerie, does hereby declare and state that:

1.   He currently works as the Head of Chemistry at Centre de Recherche Pernod Ricard,
       associated with assignee of record Pernod Ricard.

2.   His *"Curriculum Vitae"* and a "List of Publications," which listed publications he
       authored or co-authored, are attached hereto.

3.   He is familiar with the subject application and the final Office Action mailed November
       29, 2001, and Advisory Action mailed January 17, 2002, and the rejection of claims as
       set forth, therein, under 35 USC 103(a) ("the rejection") based on U.S. Pat. No. 4,966,779
       (Kirk).

4.   He provides his analysis and opinion as an expert in the art, as follows, to show that,
       contrary to allegations made in support of the rejection, one skilled in the art would not

have considered the particle size of at least 0.5 μm (500 nanometers) in the milky

emulsion taught by Kirk to teach or suggest the particle size of at most 0.1 μm (100

nanometers) in the clear microemulsion in accordance with the invention described and

claimed in the subject application:

It was well known to one skilled in the art that the size of particles in an emulsion has a direct influence on its clarity – whether the emulsion is transparent, opaque, or somewhere in between (translucent) – otherwise referred to as its *visual aspect.*

The term "microemulsion" was first used in 1959 by J. H. Schulman and co-workers to describe a transparent, quaternary emulsion obtained by progressively adding a co-surfactant to a crude, opalescent, emulsion comprising a hydrocarbon, a surfactant, and water (Rosano, H. L., "Introduction," *Microemulsion Systems,* ed. Rosano, H. L., and Clausse, M., *xv-xix,* New York, 1995) (copy attached, hereto). These *microemulsions* were found to be constituted by particle droplets having a diameter of 60-600 Å, or 0.006-0.06 μm (Rosano, at *xvi*).

Further studies of *microemulsions* confirmed that transparency may be obtained only if the particle size is smaller than 0.1 μm (Ekwall, P. et al., *Molecular Crystals and Liquid Crystals, 8,* 157-213, 1969; Clausse, M. et al., Proceedings of the World surfactant Congress, Munich, May 6-10, 1984, Kürle Druck Glenhousen, West Germany 1984, Vol. III, 209-219; Boned, C. et al., *Journal of Colloid Interface Science, 88,* 602-604, 1982) (copies of which are attached, hereto).

One skilled in the art would have typically reserved the term "microemulsion" to identify clear emulsions having droplet diameters no larger than 0.1 μm (100 nanometers) and to distinguish "emulsions," which are opaque (i.e., milky or cloudy) in appearance and have much larger droplet diameters. Moreover, one skilled in the

-2-

art would have understood that this difference in droplet size is a determinative factor in the clarity/opacity difference. As set forth in *Microemulsion: A Definition*, online at URL http://surfactants.net/microemulsion.htm (copy attached, hereto):

> *Micro*emulsions are typically *clear solutions*, as the droplet diameter is approximately *100 nanometers or less.* . . . Emulsions (or *macro*emulsions) are in contrast unstable, the suspended droplets . . . are much larger, typically one micron or more, resulting in a *cloudy or milky* dispersion. [*Emphasis added.*]

Besides the effect of particle size, the formation of a clear/quaternary microemulsion – from its milky precursor – is effected by the surface tension at the interface between oil and water in the precursor emulsion. The stability of a microemulsion obtained by adding to its precursor a co-surfactant depends on the structure of the film that coats each particle formed as the co-surfactant is added.
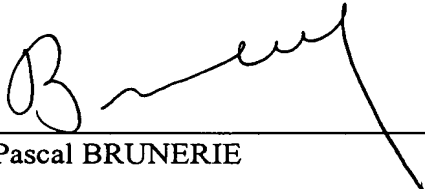
Kirk (US Pat. No. 4966779) does not disclose a *microemulsion*, either expressly or inherently. What Kirk does disclose are stable, water-miscible emulsions (i.e., *macro*emulsions) containing having a droplet particle size of 0.5-8 µm. Example 1 of Kirk describes such an emulsion as having a *milky aspect* (Kirk column 6, lines 12-13) and a droplet size of 2 µm (Kirk column 6, lines 5-6). The conspicuous absence from Kirk of any mention of the term *microemulsion* is consistent with the fact that milky emulsions having a particle size of 0.5 µm (or larger) would not have been considered *microemulsions* by one skilled in the art. On the contrary, the person skilled in the art would have considered Kirk's disclosure of particle sizes no less than 0.5 µm, being so far from the particle sizes (no larger than 100 nanometers) necessary for a microemulsion, as effectively *excluding* clear, microemulsions, i.e., as effectively *limited to* milky, non-microemulsions.

The physical phenomena managing the formation of microemulsions, in fact, teach away from the conclusion, alleged in the rejection, that the stable, cloudy emulsion having an average droplet size of about 0.5-8 μm disclosed in Kirk would have rendered obvious to one skilled in the art the stable, clear microemulsion having a diameter no larger than 0.1 :m in accordance with the invention disclosed and claimed in the subject application.

The undersigned hereby declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Further declarant sayeth naught.

03/03/04
_____
Date

_____
Pascal BRUNERIE

P64053-bruniere rule132(2nd revised).doc

-4-

BRUNERIE PASCAL
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46 years old
Married, 2 children

PROFESSIONAL EXPERIENCE

CENTRE DE RECHERCHE PERNOD RICARD

Since 2001   Head of the Chemistry Department

Budget: 360 KEuros (out the salaries)

Mission:
Conception, organisation and setting of research and use projects. Leadership of a team comprising seven persons, one engineer and five technicians.

Field of activity:
Research in the field of taste and smell applied to the products of the Group
Authenticity control of the aromas
Relationship between the sensorial properties and the aromatic composition
Determination of the origin of the raw materials
Service delivery of the Group subsidiaries

Used techniques:
Gaseous chromatography
Coupling between gaseous chromatography and mass spectrometry
High performance liquid chromatography
Atomic absorption
Isotopic mass spectrometry

Miscellaneous:
President of the Club Arômes Alimentaires de l'association ECRIN (Echange et Coordination Recherche et Industrie).
President of the Technico-Scientific Group of the CEPS (Confédération Européenne des Producteurs de Spiritueux).
Member of the Office International de la Vigne et du Vin as expert in analysis methods.
Technical auditor at the Comité Français d'Accréditation (COFRAC).
Expert member of the Commission Générale d'Unification des méthodes d'Analyse à la Direction Générale de la Concurrence, de la Consommation et de la Répression des Fraudes.

1994-2001	**Assistant of the Head of Department** Department of analytical chemistry

1990-1994   **Head of analytical chemistry laboratory**
Organisation of research and use projects
Organisation of the work of one team comprising two engineers and three technicians

1987-1990   **Research engineer in analytical chemistry**
for PERNOD RICARD

1986-1987   **Post doctoral fellow**
Würzburg University (Germany) in the laboratory of Professor SCHREIER
"Study of the biotransformation of terpenic alcohols by a grapes mould"

SCIENTIFIC EDUCATION

1981-1984   **PhD IN ORGANIC SYNTHESIS**
Université Pierre et Marie Curie (Paris VI)

1979-1981   **MAITRISE IN BIOCHEMISTRY**
DEUG de Sciences de la nature et de la vie
Université Pierre et Marie Curie (Paris VI)

LANGUAGES

. Anglais (fluent)
. German (good knowledge)

SCIENTIFIC PUBLICATIONS

Thirty articles concerning the work by PERNOD RICARD and published in journals at the Advisory Comity's

Eight patents and patent applications concerning the production of natural flavouring substances

LIST OF PUBLICATIONS

* Azabicyclic Compounds Synthesis: Reactions of Cyclic Beta-Enaminoesters with Alpha, Beta-Unsaturated Carbonyl Compounds
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Microemulsion: A Definition

A microemulsion is a thermodynamically stable dispersion of one liquid phase into another, stabilized by an interfacial film of surfactant. This dispersion may be either oil-in-water or water-in-oil. Microemulsions are typically clear solutions, as the droplet diameter is approximately 100 nanometers or less. The interfacial tension between the two phases is extremely low.

Emulsions (or macroemulsions) are in contrast unstable, the suspended droplets will eventually agglomerate and the dispersed phase will phase separate. Emulsion droplet sizes are much larger, typically one micron or more, resulting in a cloudy or milky dispersion. The nature of an emulsion may depend on the order of mixing of the ingredients and the amount of energy put into the mixing process. The final microemulsion state will not depend on order of mixing, and energy input only determines the time it will take to reach the equilibrium state.
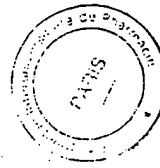
Microemulsions are two phase systems, in contrast to micellar solutions, which may be considered one phase.

For books on microemulsions and their applications, click here.

For more information on surfactants, see the Surfactants Virtual Library.

MICROEMULSION SYSTEMS

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Introduction

In reporting the proceedings concerned with "Microemulsion Systems" at the 59th Colloid and Surface Science Symposium and the 5th International Conference on Surface and Colloid Science (Potsdam, New York, June 24-28, 1985), this book also reflects the difficulty experienced by the participants in reaching a common ground on the definition of the term "microemulsions." Over 20 definitions were proposed, but no clear-cut definition emerged. The only common definition described these clear (or sometimes lactescent) systems as containing one polar liquid (generally water or saline), a hydrophobic liquid (the "oil phase"), and a selected (one or several) surface active agent.

The word "microemulsion" was originally proposed by Jack H. Schulman and co-workers in 1959, although the first paper on the topic dates from 1943. They prepared a quaternary solution of water, benzene, hexanol, and K oleate, which was stable, homogeneous, and slightly opalescent. These systems became clear as soon as a short chain alcohol was added. In the years between 1943 and 1965, Schulman and co-workers described how to prepare these transparent systems. Basically, a coarse (or macro) emulsion was prepared, and the system was then titrated to clarity by adding a cosurfactant (second surface active substance). When the combination of the four components was right, the system cleared spontaneously. Most of the work reported by Schulman dealt with four-component systems: hydrocarbons (aliphatic or aromatic); ionic surfactants; the cosurfactant, generally 4- to 8-carbon chain aliphatic alcohol; and an aqueous phase. Schulman had previously published extensively in the field of monolayers, and applied what he had learned in that field to explain the formation of a microemulsion. He proposed that the surfactant and the cosurfactant, when properly selected, form a mixed film at the oil/water interface, resulting in an

interfacial pressure exceeding the initial positive interfacial tension.
The concept of a *negative interfacial tension* was suggested by
Schulman. Rosano and co-workers showed that transitory zero (or
very low) interfacial tensions obtained during the redistribution of
the cosurfactant often play a major role in the spontaneous formation
of these systems. This conclusion was based on the differences in
the observed results when the order of mixing the components was
changed.

To summarize, the basic observation made by Schulman and co-
workers was this: when a cosurfactant is titrated into a coarse
emulsion (composed of a mixture of water/surfactant in sufficient
quantity to obtain microdroplets/oil), the result may be a system
which is low in viscosity, transparent, isotropic, and very stable.
The transition from opaque emulsion to transparent solution is
spontaneous and well defined. It was found that these systems are
made of spherical microdroplets with a diameter between 60 to 800
angstroms. It was only in 1959 that Schulman proposed to call these
systems *microemulsions*: previously, he used terms such as *trans-
parent water and oil dispersion, oleopathic hydromicelles, or hydro-
pathic oleomicelles.*

In 1943, T. P. Hoar and Jack H. Schulman describing an oil/water
system wrote: "The disperse phase consists of submicroscopic mi-
celles having a core of soap-in-water solution and a surface mono-
layer of soap ionic-pairs, interspersed with nonionized amphipathic
molecules, with the hydrocarbon portions orientated outwards. The
high soap/water ratio ensures that the soap is undissociated. The
presence of the water/oil interface containing orientated nonionized
amphipatic molecules allows undissociated soap ion-pairs also to ori-
entate there, as an alternative to association in curd filers. The
nonionized amphiphatic molecules separate the soap ion-pairs suffi-
ciently to prevent the repulsion between them that would otherwise
occur, and indeed convert the repulsion in the monolayers into an
attraction by forming complexes with the soap."

In order to explain the "spontaneous" formation of these micro-
droplets and their stability, the following explanation was advanced
by Schulman: recall that π-surface pressures can be obtained spon-
taneously by the monolayer penetration of an alkyl alcohol or choles-
terol monolayer with ionic surface active agents such as salts of
alkylsulfate and alkylamines and substituted amines injected into the
underlying solution (at constant area of the insoluble monolayer).
The value of π-surface pressures at the air/water interface can reach
values of more than 60 dynes/cm (although the collapse π-pressure
for single component monolayers on their own are below 35 dynes/cm).
If the surface pressure is held constant, or below the 60 dynes/cm
but above the 35 dynes/cm, immediate expansion of the interfacial
area takes place as the molecules of ionic surfactant penetrate the

Introduction

monolayer at the air/water interface. The analogous penetration of the mixed film by oil molecules at the oil/water interface increasing the surface area is the basis for the formation of microemulsions. However, the penetrating pressure in this case must be greater than the oil/water surface tension γ o/w, which is always less than γ a/w tension of 72 dynes/cm, which is approximately 50 dynes/cm for hydrocarbon and 35 dynes/cm for aromatic hydrocarbon compounds.

Therefore, it is progressively easier to obtain negative interfacial tensions for these systems, provided that the oil molecules can penetrate the interfacial film. Rosano et al. measured the change in the water-oil interfacial tension while alcohol was injected into one of the phases. It was found that the interfacial tension may be temporarily lowered to zero while the alcohol diffused through the interface and redistributed itself between the water and oil phases. It would therefore be possible for a dispersion to occur spontaneously (while $\gamma_i = 0$). It is then possible for the interfacial tension of a system to drop to zero for a certain period of time due to redistribution of amphiphatic molecules while the equilibrium γ_i remains positive. A sufficiently low positive value of γ_i is always better for emulsion (macro- or microemulsion) formation; nevertheless, below a certain positive small equilibrium value of γ_i phase separation, sol or gel formation will be produced but not emulsification.

Finally, stability, in turn, is not dependent on the value of the interfacial tension, but on the structure of the interfacial film surrounding the individual droplet. Therefore, low interfacial tension appears to be required for stability to occur at any degree. This finding is similar to observations of Shinoda and Saito, who first suggested forming their emulsification process using nonionic surfactants at the phase inversion temperature (PIT) where minimal interfacial tension is reached and then lowering it for further stability. At the PIT, γ_i is minimum favor to o/w interfacial area formation. In Rosano's et al. work on microemulsification, the same concept seems to apply: low interfacial tension is initially produced to lower the initial work requirement but through transfer and redistribution at the interface. Eventually the interfacial tension increases while the o/w interface curls and droplets are formed, allowing a barrier to form at the interface and preventing coalescence. This observation was also described mathematically by Defay and Sanfeld.

In order to obtain spontaneous microemulsion formation, the selection of the primary surfactant and cosurfactant and the right procedu capable of favoring redistribution between phases is important. Rosar et al. have stressed that the spontaneous formation of these dispersec swollen micelles is not dependent on simple thermodynamic stability, but rather—at least in part—on the occurrence of kinetic conditions favorable to the dispersion of the dispersed phase into the o/w system.

Essentially, the pioneering work of Schulman and later, his students, was to correlate chemical structure of the various components in the microemulsion system to their spontaneous formation. As was mentioned above, the use of the word "microemulsion" has been disputed and other labels have been preferred: transparent emulsion micellar emulsion, micellar solution, swollen micellar solution. Those who prefer to use micellar solution or swollen micellar solution consider the fact that systems of the same kind are made of one surfactant with double chain (sodium dioctylsulfosuccinate-Aerosol OT). It is possible to obtain a microemulsion-type system by either incorporating a hydrocarbon into the aqueous micellar solution or putting water into an organic solution containing the surfactant (*inverse micelles*). For these authors, microemulsion formation must be considered a micellization or micellar solubilization process of a macroemulsion when a selected cosurfactant is added. Winsor has described and studied monophasic media composed of water/organic salt/additives/hydrocarbon. He has described these systems as "solubilized." On the other hand, Friberg et al. and several others have, from the analysis of phase diagrams, underscored the fact that systems studied by Schulman (water/surfactant/cosurfactant/oil) evolve from ternary monophasic solutions (water/ionic surfactant/alcohol).

In the final analysis, there is no real opposition to the concept of microemulsion versus swollen micellar solution. It seems that the word "microemulsion" is used more often to describe any multicomponent fluids made of water (or a saline solution), a hydrophobic liquid (oil), and one or several surfactants, these systems being stable, with a low viscosity, transparent, and isotropic. On the one hand, from an application point of view, "spontaneous" formation of these systems (high energy drinks, O_2-carrier, imaging solutions, inks, household and personal care products, and so on) remains an important characteristic. On the other hand, from a purely scientific point of view a so-called microemulsion fluid may exist as one phase of mutual solubilization of all the components. It may also constitute one phase of a polyphasic system. The other phases can either be water or organic phases in excess (Winsor systems), or mesophases (lytropic liquid crystals). With certain polyphasic systems, two such phases may be of the microemulsion type. It should be noted that the word "microemulsion" has been used to describe media with no strong amphiphile (waterless microemulsions) and also media where formamide or glycerol were used instead of water. The lack of discrimination in the use of a precise definition of the word "microemulsion" may be unacceptable to some but it has not prevented people from investigating these systems. We must be grateful to the late Jack H. Schulman for offering such a catchy word to his colleagues. Maybe the ambiguity of this word, which is easy to

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remember, has helped to awaken the scientific and industrial world
to consider the fundamental and practical applications of these sys-
tems. To be sure, the word has helped to some degree to stimulate
research on these systems, and it is hoped that this book will en-
courage more.

On June 20, 1967, the announcement of the tragic death of
Jack H, Schulman, Professor at Columbia University, came
as a great shock to his many friends and colleagues. We in the
field of colloid and interface science hold him in high esteem for
his impressive record of important achievements. It is fitting
for us to dedicate this book to his memory.

Henri L. Rosano

LETTER TO THE EDITORS

Partition of the W/O Area of Winsor IV Phases

Within the realm of existence of quaternary water/ionic surfactant/alcohol/hydrocarbon w/o Winsor IV phases (so-called inverted microemulsions), the electrical conductivity undergoes non-monotonous variations as the composition varies. In the general case, it is possible to define two lines, Γ_1 from conductivity maxima and Γ_2 from conductivity minima. Γ_1 and Γ_2 partition the w/o Winsor IV realm into three adjacent subareas, PM, ME, and MC, that can be assigned compositions corresponding, respectively, as the water content increases, to premicellar hydrated surfactant aggregates, inverted swollen spherical micelles, and micelle clusters. A similar behavior is put into evidence for ternary Winsor IV phases made up of water and dodecane with the well-balanced ionic surfactant Aerosol OT as the surface active agent. In some cases, Γ_2 cannot be defined and, consequently, it is not possible to identify the MC subarea.

Winsor IV phases (1), commonly called microemulsions after Schulman *et al.* (2), are macroscopically monophasic, fluid, transparent, and isotropic media made up by mixing within adequate proportions water and a hydrocarbon in presence of suitable amphiphilic substances, very often combinations of an ionic surfactant and of a medium chain-length alcohol (cosurfactant). During the past decade, intensive investigations have been devoted to Winsor IV phases which belong to the class of short-range organized fluids and exhibit interesting properties in view of applications in many industrial fields (3–6).

A most useful representation for quaternary Winsor IV systems incorporating a surfactant–alcohol combination (defined by k, the surfactant/alcohol mass ratio), is the WHS mass pseudoternary phase diagram, on which it is possible to delineate the realm of existence of Winsor IV phases (monophasic domain). Two different main situations can be encountered, depending upon composition factors such as the alcohol molecular structure (7). For a first class of systems (Type I), the water-in-hydrocarbon (w/o), and hydrocarbon-in-water (o/w), areas merge so as to form a unique Winsor IV domain. In that situation, the Winsor IV phases exhibit a fairly high electrical conductivity whose variations at low and medium water contents can be described by means of equations derived from the Percolation and Effective Medium theories (8). For a second class of systems (Type II), the w/o and o/w areas are disjoined and separated by a composition zone over which long-range organized media are encountered. This situation, depicted here by the phase diagrams of Figs. 1 and 2, is similar to that prevailing in the case of ternary Winsor IV phases incorporating a well-balanced surfactant such as Aerosol OT (AOT), instead of a surfactant–alcohol combination, as illustrated by Fig. 3. In that situation, over the w/o area, the electrical conductivity of the Winsor IV phases keeps low values and undergoes non-

monotonous changes as the system composition varies (7, 9).

In a preceding paper (9), it was shown, on the Type II system water/potassium oleate/1-hexanol/hexadecane, that the electrical conductivity nonmonotonous changes allowed to partition the w/o area into three adjacent subareas, by means of two lines Γ_1 and Γ_2 defined by compositions corresponding, respectively, to conductivity maxima and minima. In an attempt to ascertain and generalize this result, a more complete study has been carried out on several Type II systems made up of different hydrocarbons, surfactants, and alcohols. The experimental procedure followed was described in detail previously (9).
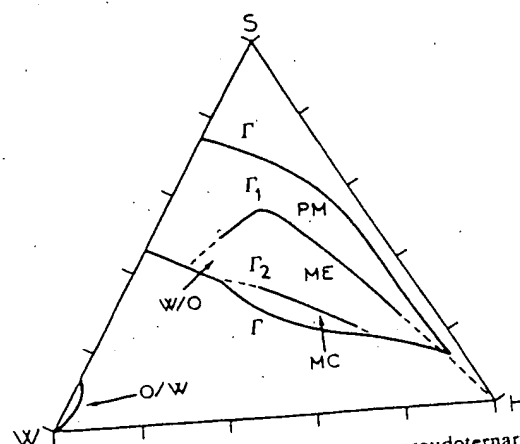

FIG. 1. w/o Winsor IV area in the mass pseudoternary phase diagram of water/potassium oleate/1-pentanol/benzene systems, at $T = 298$ K. W, 100% water; H, 100% hydrocarbon; S, 100% surface active combination (surfactant/alcohol mass ratio k equal to 3/5).
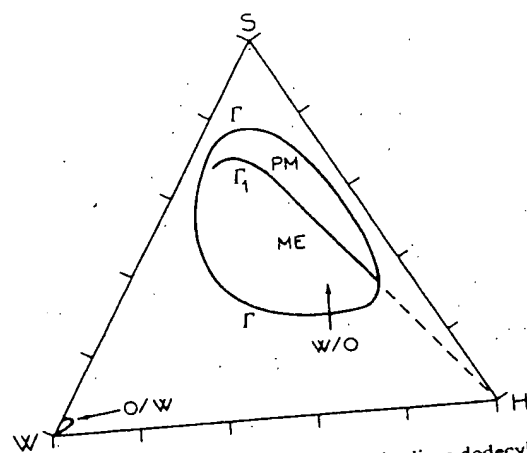
FIG. 2. w/o Winsor IV area of water/sodium dodecyl sulfate/1-heptanol/dodecane systems, at $T = 298$ K ($k = 1/2$).

Among the six systems investigated, three of them (water/sodium dodecyl sulfate/1-hexanol/dodecane; water/sodium dodecyl sulfate/1-pentanol/benzene; water/potassium oleate/1-pentanol/benzene) displayed a conductive behavior of their w/o Winsor IV phases similar to the one put into evidence previously on the water/potassium oleate/1-hexanol/hexadecane system. From the compositions corresponding to conductivity maxima and minima, it was possible to define two lines, Γ_1 and Γ_2, respectively, that partition the w/o Winsor IV area into three adjacent subareas that are labeled PM, ME, and MC in Fig. 1. For the other three systems (water/sodium dodecyl sulfate/1-heptanol/dodecane and water/sodium dodecyl sulfate/1-hexanol or 1-hep-

tanol/benzene), the line Γ_2 was not identified clearly since the composition points corresponding to conductivity minima fell on or very close to the lower branch of the boundary Γ of the w/o Winsor IV area. In that case, the w/o monophasic area is partitioned by Γ_1 into two adjacent subareas labeled PM and ME in Fig. 2:

The different conductivity trends observed can be ascribed to structural changes in the w/o Winsor IV phases as the composition varies (9). Over the subarea labeled PM, the water/surfactant ratio is low and it is most likely that the systems consist of suspensions of hydrated surfactant premicellar aggregates. As shown on Figs. 1 and 2, Γ_1 presents a linear portion, directed toward the H apex of the phase diagram, which indicates a constant water/surfactant molar ratio x_w/x_s that was evaluated to 12 or so in the case of water/sodium dodecyl sulfate/1-heptanol/dodecane systems (Table I). This finding is consistent with results reported by other authors (10-12). Γ_1 can be considered as a curve marking the onset of formation of stable inverted swollen spherical micelles that exist all over the subarea labeled ME and bounded by Γ_1 and Γ_2 (Fig. 1), or Γ_1 and the lower branch of Γ when Γ_2 does not exist (Fig. 2). By introducing $\bar{\sigma}$, the average area per surfactant molecule polar head, it is possible to compute micellar parameters from the constant value of x_w/x_s. In the case of water/sodium dodecyl sulfate/1-heptanol/dodecane systems, the water core radius r_w and the micelle radius r_m were found equal respectively to 52 and 73 Å or so (Table I), values that agree with data reported in the literature. Below Γ_2, when this curve can be defined, the conduc-

TABLE I

Composition and Micellar Parameters along Γ_1 for the Water/Sodium Dodecyl Sulfate/1-Heptanol/Dodecane System (Surfactant/Alcohol Mass Ratio: $k = 1/2$)

p_a[a]	$(p_w)_a$[b]	p_s[c]	x_w/x_s[d]	r_w[e]	r_m[f]
0.06	0.250	0.230	17	77	98
0.07	0.225	0.235	15	68	89
0.15	0.180	0.223	13	59	80
0.20	0.165	0.212	12	54	75
0.30	0.128	0.191	11	50	71
0.40	0.113	0.163	11	50	71
0.50	0.095	0.135	11	50	71
0.57	0.085	0.115	12	54	75

[a] Dodecane mass fraction.
[b] Water mass fraction.
[c] Sodium dodecyl sulfate mass fraction.
[d] Water/surfactant molar ratio.
[e] Water core radius (in Å).
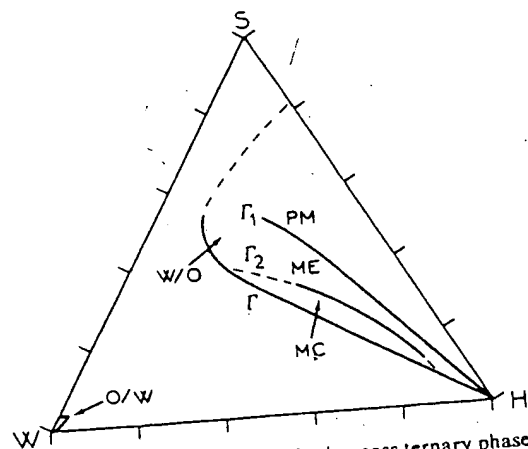[f] Micelle radius (in Å).

FIG. 3. w/o Winsor IV area in the mass ternary phase diagram of water/Aerosol OT/dodecane systems, at $T = 298$ K.

LETTER TO THE EDITORS

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tivity sudden increase with water content suggests the apparition of nonspherical entities, either elongated micelles or, more likely, micelle clusters resulting from a clustering process induced by attractive interactions between swollen w/o micelles (13, 14). As illustrated by Fig. 3, for ternary systems formed with water, a hydrocarbon and a well-balanced ionic surfactant such as AOT, similar phenomena can be observed, with values of x_w/x_s along the linear part of Γ_i equal to 11 or so and values of r_w and r_m equal to 20 and 31 Å, respectively, which is in good agreement with structural data obtained from other techniques (15). All these results will be presented and commented upon in detail in a forthcoming full article.

ACKNOWLEDGMENTS

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English Translation
&
Original (French language)

*Systèmes eau/composés
amphiphiles/hydrocarbure.
Utilité des etudes de diagrammes des phases*

$\left\{\begin{array}{c} \textit{Water/amphiphilic compound/hydrocarbon systems.} \\ \textit{Value of phase diagram studies} \end{array}\right\}$

M. Clausse, L. Nicolas-Morgantini, A. Zradba

constituents, temperature, optionally pressure, etc.),
on the behaviour of the system. By means of comparative
analyses of the phase diagrams of similar systems, it
is possible to demonstrate the influence of various
compositional parameters on the formation and stability
or the equilibrium of media comprising mesophases
and/or phases of the microemulsion type. Such studies
are of immediate usefulness as regards the
technological and industrial applications of systems
containing amphiphilic compounds. In general, they lead
towards the establishment of a typology of the mode of
action of the various classes of amphiphilic compounds,
used alone or in combination, and thus of their
capacity to induce the formation either of a mesophase
or of unordered phases of the microemulsion type. In
the case in point, they make it possible to obtain
precise knowledge of the conditions for obtaining a
given type of medium, this information being, on
account of the appreciable differences in physical
properties (for example viscosity) presented by
mesophases and microemulsions, of great importance for
the design of industrial processes based on the use of
multi-constituent complex fluids, some constituents of
which are of the amphiphilic compound type. For largely
identical reasons, the study of phase diagrams is also
of great value in the field of fundamental research
devoted to systems containing amphiphilic compounds.
With the information that it provides regarding the
internal organization of phase diagrams, this method
makes it possible to identify general behaviour models,
especially as regards the modes of transition between
media of different species, and to develop, where
appropriate, particular situations possibly revealing
the existence of media of "eccentric" structure.
However, the phase diagram method, used alone, can give
only general indications, which are insufficient to
gain access to precise knowledge of the various types
of medium. It can therefore be a fertile method only if
it is combined with techniques for obtaining a detailed

Water/amphiphilic compound/hydrocarbon systems.
Value of phase diagram studies

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Mixtures of water (or aqueous saline solution)/amphiphilic compounds/hydrocarbon(s) give rise to media that are very varied in the number and nature of the various macroscopic phases of which they are composed, when thermodynamic equilibrium is reached. The most advantageous situations are those for which the medium comprises at least either a mesophase, (1), i.e. a phase with wide-scope organization, or a microemulsion, (2), i.e. an unordered fluid phase, rich in amphiphilic compounds, which may incorporate large amounts of water and/or of hydrocarbon. The study, as a function of the composition and the thermodynamic constraints, of the formation of media comprising mesophases and/or microemulsions and of the configuration of the stability range of these particular phases (in the case of one-phase media), or of equilibrium of these particular phases with each other or with excess aqueous and/or organic phases (in the case of multi-phase media), is a subject of great interest, from both a strictly scientific and a technical point of view.

An examination of the abundant literature devoted to mesophases and microemulsions shows that the study of these media may be performed using very varied methods, some of which are based on sophisticated techniques. A standard method for studying systems containing amphiphilic compounds consists in determining and analysing the internal organization of their phase diagrams. For a given system, this method makes it possible to delimit the regions of existence of the various possible types of medium and to demonstrate the influence of diverse variables (titres of the various

description of the structure of the media and of the
interactions existing therein. The structure of
mesophases may be determined by means of X-ray
diffraction experiments (3-5), preceded or
complemented, as necessary, by observation of the
optical textures, using a polarizing microscope or an
electron microscope, and by measuring certain physical
properties, such as the density, the viscosity and the
electrical conductivity (6-8). Details of the
organization of these media may be obtained using
techniques such as nuclear magnetic resonance, electron
paramagnetic resonance and small-angle neutron
scattering (7, 9-11). As regards unordered phases of
the microemulsion type, studies aimed at determining
their structure are very numerous and varied, in terms
of both the nature of the systems and the objectives
pursued and techniques used. This may be illustrated
with the example of water/ionic
surfactant/alcohol/hydrocarbon quaternary systems. In
the case of systems of this type, various groups of
authors have proposed, for one-phase microemulsions low
in water but saturated with hydrocarbon, models of
internal structure and interactions (12-14), these
models being based on results obtained from ultra-
centrifugation, small-angle neutron scattering,
electroconductimetry, viscometry and light-scattering
experiments (12, 15-21). These models constitute a
solid basis for the development of research aimed at
identifying the structure of non-saturated one-phase
microemulsions, over their entire range of existence,
and also that of microemulsions consisting of the
phases rich in amphiphilic compounds of "Winsor" two-
phase and three-phase media (22). Since the dilution
process used in the case of saturated microemulsions,
which is a process that is said to have no effect on
their structure and the interactions existing therein
(23), cannot be applied to saturated one-phase
microemulsions and to the microemulsions of Winsor
systems, study of the structure of these dense media

cannot in fact be performed in the same manner as that of the structure of saturated microemulsions. The studies devoted to non-saturated one-phase microemulsions generally consist in monitoring the evolution of a certain number of physicochemical characteristics of the medium as a function of various compositional parameters (24). The results thus obtained are analysed globally, by direct or indirect reference to the phase diagram of the systems under consideration, which makes it possible to draw conclusions regarding the structure of the medium in different regions of the microemulsion domain. It is thus possible to check whether the structural models developed in the case of saturated microemulsions can be transposed to the case of non-saturated one-phase microemulsions or whether new models allowing the various experimental data to be taken into account should be developed. It is along similar lines that the structure studies relating to phases rich in amphiphilic compounds of multi-phase media of the Winsor type are performed, (25). This is also true in the case of other categories of systems, such as systems containing nonionic amphiphiles or systems containing only one ionic amphiphile of the Aerosol OT type, with which one-phase microemulsions and media of the Winsor type are also obtained.

The literature abounds with examples demonstrating the value of the phase diagram method for the experimental study of microemulsions. Some of these are briefly reported hereinbelow, as illustrations. Shinoda et al. (26-33) performed numerous studies concerning the phase diagrams of systems containing nonionic surfactants. This enabled them to show the influence, on the behaviour of systems of this category, of the nature of the surfactant, of that of the hydrocarbon and of that of additives of the electrolyte type, and to demonstrate very clearly the decisive influence of temperature on the activity of the surfactant and thus

on the formation and the stability range of a given type of medium. The numerous data thus acquired allowed the authors to define the conditions required to obtain one-phase microemulsions incorporating large amounts of water or hydrocarbon. By applying the same method of study, Kunieda and Shinoda (34-35) showed that the behaviour of systems incorporating Aerosol OT as sole amphiphile is globally analogous to that of systems containing nonionic surfactants. In the course of their studies, Shinoda et al. paid most particular attention to the effect of temperature on the behaviour of systems containing nonionic surfactants. This led them, as a general rule, to consider as a parameter the concentration of the surfactant in the systems and thus to determine the organization of the phase diagrams of the systems studied as a function of two variables, the temperature and the relative water (or hydrocarbon) content. For reasons associated with the general objectives of their studies, Shinoda et al. essentially studied systems characterized by surfactant concentration values of the order of or less than 10%, which, in a certain manner, limits the general scope of the results obtained by these researchers. Other authors adopted a complementary approach by treating the temperature as a parameter, which led them to determine, at a given temperature, phase diagrams as a function of the concentrations of the three basic constituents of the systems: water, hydrocarbon and nonionic surfactant. Examples that may be mentioned include the studies by Lo et al., (36), Hermann et al., (37-38), Mathis et al., (39), Boyle et al., (40) and Friberg et al., (41-42). The results acquired by these authors show that, in the water/surfactant/hydrocarbon ternary diagram, the configuration of the domain of existence of media of the microemulsion type varies enormously as a function of certain parameters, such as the nature of the hydrocarbon or the temperature. The results obtained by Mathis et al., (39), Boyle et al., (40), and Friberg et al., (41-42), show that, in the

concentration-temperature three-dimensional diagram of
the systems studied, the domain of existence of media
of the microemulsion type is contiguous, which makes it
possible to understand why, following the temperature
value, the microemulsion domain determined in the
water/surfactant/hydrocarbon ternary diagram may
consist either of a single region or of two or three
detached regions. Nilsson and Lindman, (43), exploited
this experimental finding to attempt, via nuclear
magnetic resonance experiments, to determine the
structure of the medium in the various microemulsion
regions of three heavy water/surfactant/hydrocarbon
systems similar to those studied by Friberg et al.,
(41-42). The results thus obtained as regards the
variations, as a function of the composition, of the
coefficients of autodiffusion of the heavy water, of
the hydrocarbon and of the surfactant tend to show
that, over the majority of the microemulsion domain,
there are no clearly structured water/hydrocarbon
interfaces and that the formation of Schulman
microemulsions, (2), i.e. dispersions of microdroplets
of water in organic medium or of microdroplets of
hydrocarbon in aqueous medium, takes place only in
regions corresponding to compositions that are very
rich in hydrocarbon or very rich in water. As regards
systems incorporating ionic surfactants, the studies of
Ekwall et al., (1), should firstly be recalled, which
constitute a reference since they form a quite full
catalogue of the various types of internal organization
of phase diagrams of systems comprising an organic
body, an ionic surfactant and water. The diagrams
published by these authors show especially that the
domain of existence of media of the microemulsion type
may have a very varied configuration, which depends on
the nature of the organic substance and on that of the
ionic surfactant. Various groups of authors have
devoted part of their studies to determining the
microemulsion domains of standard water/ionic
surfactant/alcohol/hydrocarbon quaternary systems,

which is considered as the starting point for microemulsions of this type. In order to demonstrate the relationships existing between quaternary microemulsions and water/ionic surfactant/alcohol ternary one-phase solutions, Friberg and coworkers, (44-47), quite exhaustively studied the water/potassium oleate/1-hexanol/benzene system, by combining various techniques with the phase diagram method. They were thus able to show, firstly, that the domain of existence of microemulsions of the water-in-hydrocarbon type of the system under consideration ("inverse" microemulsions) constitutes the three-dimensional development of the domain of existence of water-in-alcohol one-phase solutions ("inverse" micellar solutions L_2), secondly, that inverse microemulsions and inverse micellar solutions show behavioural analogies as regards the change of some of their physicochemical properties with the water content. It appears in particular that inverse micellar solutions and microemulsions are, for low water contents, suspensions in organic medium of premicellar aggregates, formed from water molecules strongly bound to surfactant molecules, and do not contain true microdroplets of water, with an aqueous core surrounded by an interfacial film of surfactant and alcohol molecules, except for water contents characterized by a water/surfactant molar ratio of greater than about 10. From these results, Friberg et al. drew the conclusion that there is structural continuity between inverse micellar solutions and inverse microemulsions. Other authors have also arrived at this conclusion (48). The relationships existing between quaternary microemulsions of the hydrocarbon-in-water type ("direct" microemulsions) and alcohol-in-water one-phase solutions ("direct" micellar solutions L_1) were also studied by Friberg and coworkers, (49-53). The results obtained show that the formation and stability of direct microemulsions are complex phenomena on which certain compositional parameters such as the

water/surfactant ratio and the nature of the hydrocarbon have a very pronounced influence. Podzimek and Friberg, (51), found that certain direct microemulsions are not thermodynamically stable, which is in line with observations reported by other authors, (54-57). Phase diagrams published by Friberg and coworkers, (51-52), show that the three-dimensional domain corresponding to the existence of direct microemulsions may have a convoluted configuration, which explains the diversity of configuration presented by the direct microemulsion regions in pseudo-ternary diagrams defining cross-sections of the three-dimensional microemulsion domain, as a function of a given parameter. This is in line with observations regarding the configuration of the microemulsion domains of certain systems containing nonionic surfactants (39-42). It may incidentally be recalled in this respect that Shinoda et al., (58), showed that there are similarities between phase diagrams of systems containing nonionic surfactants and phase diagrams of systems containing combinations of an ionic surfactant and of a cosurfactant. An important experimental fact that emerges from the results of Friberg and coworkers, (51-53), is that the direct microemulsion domain may extend as far as regions of the phase diagram corresponding to compositions in which the hydrocarbon is markedly the predominant constituent. The possibility, thus demonstrated by phase diagram studies, of forming "direct" media with a very high hydrocarbon content is encouragement for undertaking researches concerning their exact nature and the conditions required for their formation and their stability, the results of this research potentially being of great interest, both scientifically and technically. Determinations of microemulsion domains of water/ionic surfactant/alcohol/hydrocarbon quaternary systems were performed by Bellocq et al., (24, 59-64), who used them as a support for structural studies using varied

techniques (viscometry, electroconductimetry, nuclear magnetic resonance and relaxation, electron micrography, light scattering and vapour tension measurements). The extensive experimental data thus acquired show that non-saturated microemulsions have large structural diversity and that structural transitions take place gradually when the composition of the medium varies. It appears that, in certain regions of the microemulsion domain, the structure of the medium may be unambiguously identified (populations of microdroplets of water or of hydrocarbon, or premicellar aggregates). On the other hand, it appears that, in other regions such as the "central" portion of the microemulsion domain, the structure of the medium is poorly defined, the experimental data tending to indicate that the water/hydrocarbon interfaces are poorly structured. Similar findings have been reported by other authors (65-70). Bellocq et al., (71-74) also determined the organization of the phase diagrams of systems giving rise to varied multiphase media containing phases of the microemulsion type. Studies of the behaviour of these multi-phase media and of the properties of their phases of the microemulsion type were undertaken, which show the existence of criticity phenomena.

The studies recalled above as examples demonstrate the value and fertility of studies of phase diagrams of systems containing amphiphilic compounds, especially when they are combined with studies aimed at determining, by means of varied techniques, the structure and physical chemical properties of various types of media obtained, whether they are mesophases or phases of the microemulsion type. General information regarding the structure of non-saturated one-phase microemulsions or of microemulsions belonging to multiphase media maybe obtained relatively simply by correlating results of studies of phase diagrams and results of studies of transport properties (viscosity,

electrical conductivity, diffusion coefficients, etc.).
This method was used by Bennett el al., (75) to study,
in the case of systems containing ionic surfactants and
alcohols, microemulsions consisting of surfactant-rich
phases of two-phase and three-phase systems of the
Winsor type, (22). The results thus obtained, in
particular those concerning the viscosity and the
electrical conductivity, led these authors to conclude
that, in the course of the WinsorI → WinsorIII →
WinsorII transition induced by increasing the salinity
of the aqueous phase, the microstructure of the
surfactant-rich phase changes gradually. For the lowest
and the highest salinities, the surfactant-rich phase
is considered to be a Schulman microemulsion (2), i.e.
a population of microdroplets of the
hydrocarbon-in-water type (low salinities) or a
population of microdroplets of the water-in-hydrocarbon
type (high salinities). For intermediate salinities,
especially those inducing the formation of a
three-phase medium of the Winsor type, the
surfactant-rich phase is thought to be a dynamic mosaic
of aqueous and organic microdomains separated by very
flexible interfacial films, which is the situation that
was modelled by Scriven and other authors, (76-80),
under the name "bicontinuous structure". This is also
the method that was applied by different groups of
authors to the study of non-saturated one-phase
microemulsions of systems containing ionic surfactants
and alcohols. As examples of studies of autodiffusion
phenomena coupled with phase diagram studies, mention
may be made of the work, already mentioned, of Lindman
et al., (68-70) and that of Larche et al., (81), who
also studied the phenomenon of electrical conduction in
non-saturated microemulsions. Without having explicitly
determined the phase diagrams, Shah and coworkers,
(82-88), studied, as a function of the composition, the
viscosity, the electrical conductivity and the
permittivity of non-saturated one-phase microemulsions,
with a view to obtaining information concerning their

structure. Complementary to permittivity and electrical conductivity studies on non-saturated one-phase microemulsions, Clausse et al., (89-101) proceeded to the determination of the microemulsion domains of numerous water/ionic surfactant/alcohol/hydrocarbon quaternary systems. This enabled these authors to establish correlations between the configuration of the microemulsion domain and the electroconductive behaviour of the microemulsions, and to delimit, within the microemulsion domain, regions possibly corresponding to various types of structures. The results published by Clausse et al., (89-101) relating to water/ionic surfactant/paraffinic alcohol/hydrocarbon systems, incorporating various surfactants, alcohols and hydrocarbons but characterized by a given value, of the order of 1/2, of the surfactant/alcohol mass ratio, were able to be generalized by means of a detailed analysis of the configuration of the microemulsion domain in the tetrahedron of the phases of four water/sodium dodecyl sulphate/alcohol/n-dodecane model systems, incorporating one or other of the following four alcohols: 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol, (102). In complement, viscometry and electroconductimetry experiments were performed, aimed at allowing an identification of the structure of microemulsions in different regions of their domains of existance. This study, the detailed results of which will be published in future articles, (103-106), made it possible to demonstrate that the general configuration of the three-dimensional microemulsion domain of a water/surfactant/alcohol/hydrocarbon quarternary system is essentially conditioned by that of the mutual solubilization domain of water, of the surfactant and of the alcohol. It appears in particular that, in the case of systems incorporating a long alcohol (1-hexanol or 1-heptanol, for the systems under consideration), the direct microemulsion ↔ inverse microemulsion transition ("phase inversion") always

takes place via either multi-phase media containing isotropic phases (media of the "Winsor" type (22)) or mesomorphic media or media comprising a mesomorphic phase, whereas, in the case of systems incorporating a short alcohol (1-butanol or 1-pentanol for the systems under consideration), the phase inversion may take place diffusively, without causing any discontinuities in the macroscopic properties of the medium, since there are experimental pathways lying entirely in the microemulsion domain and connecting the water-rich regions of the compositions to the hydrocarbon-rich regions of the compositions. The existence of two categories of systems is very clearly confirmed by the results of the study of the rheological and electroconductive behaviour of the microemulsions, on which, all factors being otherwise equal, the length of the alcohol molecule has a considerable influence. In the case of systems incorporating a short alcohol, the electrical conduction in the microemulsions appears to result from a percolation phenomenon, (107), the electrical conductivity increasing, first very quickly, according to a scalar law, and then slowly, with the water content. This phenomenon does not exist in the case of systems incorporating a long alcohol, the electrical conductivity over the region of existence of the inverse microemulsions maintaining low values (of the order of 5×10^{-3} Sm^{-1}) and varying non-monotonously with the water content. An analysis of this electroconductive behaviour, which may be explained from a model proposed by Eicke and Denss, (108), leads to the suggestion that the inverse microemulsion domain of systems containing long alcohols comprises a region of existence of premicellar aggregates (low water contents) and a region of existence of true inverse emulsions, i.e. of microdroplets comprising an aqueous core delimited by a film of surfactant and alcohol molecules, and dispersed in an essentially organic phase. In parallel, the experiment shows that the rheological behaviour of microemulsions comprising a

short alcohol is very different from that of micro-
emulsions comprising a long alcohol. This combination
of results, relating to water/sodium dodecyl
sulphate/1-butanol, 1-pentanol, 1-hexanol,
1-heptanol/n-dodecane systems, is coherent with
experimental and theoretical data concerning the
structure of microemulsions and the interactions
existing therein, (12-21).

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Systèms eau/composés
amphiphiles/hydrocarbure
Utilité des etudes de diagrammes des phases

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Systèmes eau/composés amphiphiles/hydrocarbure. Utilité des études de diagrammes des phases

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Les mélanges eau (ou solution saline aqueuse)/composés amphiphiles/hydrocarbure(s) donnent naissance à des milieux très variés par le nombre et la nature des diverses phases macroscopiques dont ils sont constitués, lorsque l'équilibre thermodynamique est atteint. Les situations les plus intéressantes sont celles pour lesquelles le milieu comporte au moins soit une mésophase, (1), c'est-à-dire une phase présentant une organisation à grande portée, soit une microémulsion, (2), c'est-à-dire une phase fluide non-ordonnée, riche en composés amphiphiles et pouvant incorporer de grandes quantités d'eau et/ou d'hydrocarbure. L'étude, en fonction de la composition et des contraintes thermodynamiques, de la formation de milieux comportant des mésophases ou/et des microémulsions et de la configuration du domaine de stabilité de ces phases particulières, (dans le cas de milieux monophasiques), ou d'équilibre de ces phases particulières entre elles ou avec des phases d'excès aqueuses ou/et organiques, (dans le cas de milieux polyphasiques), constitué un sujet d'un grand intérêt, tant du point de vue strictement scientifique que du point de vue technique.

Un examen de l'abondante littérature consacrée aux mésophases et microémulsions montre que l'étude de ces mileux peut être effectuée en recourant à des méthodes très variées, dont certaines reposent sur des techniques sophistiquées. Une méthode classique d'étude des systèmes à composés amphiphiles consiste à déterminer et à analyser l'organisation interne de leurs diagrammes des phases. Pour un système donné, cette méthode permet de délimiter les régions d'existence des différents types de milieu possibles et de mettre en évidence l'influence de diverses variables, (titres des divers constituants, température, éventuellement pression,...), sur le comportement du système. Grâce à des analyses comparatives des diagrammes de phases de systèmes analogues, il est possible de mettre en évidence l'influence de divers paramètres de composition sur la formation et la stabilité ou l'équilibre de milieux comportant des mésophases et/ou des phases du type microémulsion. De telles études sont d'une utilité immédiate en ce qui concerne les applications technologiques et industrielles des systèmes à composés amphiphiles. D'une façon générale, elles conduisent à établir une typologie du mode d'action des différentes classes de composés amphiphiles, employés seuls ou combinés entre eux, et donc de leur propension à induire la formation soit de mésophase, soit de phases non-ordonnées du genre microémulsion. Sur cas d'espèce, elles permettent d'obtenir une connaissance précise des conditions d'obtention de tel ou tel type de mileu, information qui, en raison des différences notables de propriétés physiques, (viscosité, par exemple), que présentent mésophases et microémulsions, est d'une grande importance pour la conception

de procédés industriels fondés sur l'utilisation de fluides complexes à constituants multiples, dont certains sont du genre composé amphiphile. Pour des raisons sensiblement identiques, l'étude des diagrammes des phases est également d'une grande utilité dans le domaine des recherches fondamentales consacrées aux systèmes à composés amphiphiles. Par la connaissance qu'elle donne de l'organisation interne des diagrammes des phases, cette méthode permet de dégager des modèles généraux de comportement, notamment en ce qui concerne les modes de transition entre milieux d'espèces différentes, et de mettre en évidence, le cas échéant, des situations particulières pouvant révéler l'existence de milieux à structure «excentrique». Toutefois, la méthode des diagrammes de phases, utilisée seule, ne peut fournir que des indications d'ordre général qui sont insuffisantes pour accéder à une connaissance précise des différents types de milieux. Elle ne peut donc être une méthode féconde que si elle est associée à des techniques permettant d'obtenir une description détaillée de la structure des milieux et des interactions qui existent en leur sein. La structure des mésophases peut être déterminée grâce à des expériences de diffraction des rayons X, (3—5), précédées ou complétées, en tant que de besoin, par l'observation des textures optiques, au microscope polarisant ou au microscope électronique, et par des mesures de certaines propriétés physiques, telles que masse volumique, viscosité et conductivité électrique, (6—8). Des détails de l'organisation de ces milieux peuvent être obtenus en recourant à des techniques telles que la résonance magnétique nucléaire, la résonance paramagnétique électronique et la diffusion des neutrons aux petits angles, (7,9—11). En ce qui

concerne les phases non-ordonnées du genre microémulsion, les études destinées à déterminer leur structure sont très nombreuses et variées, tant par la nature des systèmes que par les objectifs poursuivis et les techniques utilisées. On peut illustrer cela par l'exemple des systèmes quaternaires eau/surfactant ionique/alcool/hydrocarbure. Dans le cas de systèmes de ce type, divers groupes d'auteurs ont proposé, pour les microémulsions monophasiques pauvres en eau mais saturées en hydrocarbure, des modèles de structure et d'interactions internes, (12—14), modèles fondés sur des résultats acquis par des expériences d'ultracentrifugation, de diffusion des neutrons aux petits angles, d'électroconductimétrie, de viscosimétrie et de diffusion de la lumière, (12, 15—21). Ces modèles constituent une base solide pour le développement de recherches visant à identifier la structure des microémulsions monophasiques non-saturées, sur tout leur domaine d'existence, et ainsi que celle des microémulsions constituées par les phases riches en composés amphiphiles des milieux diphasiques et triphasiques dits «de Winsor», (22). Le procédé de dilution utilisé dans le cas de microémulsions saturées, procédé réputé n'avoir pas d'incidence sur leur structure et les interactions existant en leur sein, (23), ne pouvant être appliqué aux microémulsion monophasiques saturées et aux microémulsions des systèmes de Winsor, l'étude de la structure de ces milieux denses ne peut en effet être effectuée de la même façon que celle de la structure des microémulsions saturées. Les études consacrées aux microémulsions monophasiques non-saturées consistent généralement à suivre l'évolution d'un certain nombre de caractéristiques physico-chimiques du milieu en fonction de divers paramètres de

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composition, (24). Les résultats ainsi obtenus sont analysés de façon globale, par référence, directe ou indirecte, au diagramme des phases des systèmes considérés, ce qui autorise à formuler des conclusions sur la structure du milieu dans différentes régions du domaine de microémulsion. On peut ainsi vérifier si les modèles structureaux élaborés dans le cas des microémulsions saturées peuvent être transposés au cas des microémulsions monophasiques non-saturées ou s'il convient de développer de nouveaux modèles permettant de rendre compte des diverses données expérimentales. C'est selon des démarches analogues que sont effectuées les études de structure relatives aux phases riches en composés amphiphiles de milieux polyphasiques du type Winsor, (25). Cela est également vrai dans le cas d'autres catégories de systèmes, tels que les systèmes à amphiphiles non-ioniques ou les systèmes à un seul amphiphile ionique du genre de l'Aérosol OT, avec lesquels on obtient aussi des microémulsions monophasiques et des milieux du type Winsor.

La littérature abonde d'exemples démontrant l'utilité que la méthode des diagrammes de phases présente pour l'étude expérimentale des microémulsions. Certains d'entre eux sont brièvement rapportés ci-dessous, à titre d'illustrations. Shinoda et collaborateurs, (26–33), ont effectué de nombreux travaux concernant les diagrammes de phases de systèmes à surfactants non-ioniques. Cela leur a permis de montrer l'influence, sur le comportement des systèmes de cette catégorie, de la nature du surfactant, de celle de l'hydrocarbure et de celle d'additifs du genre électrolyte, et de mettre en évidence de façon très nette l'influence décisive de la température

sur l'activité du surfactant et donc sur la formation et le domaine de stabilité de tel ou tel type de milieu. Les nombreuses données ainsi acquises ont permis aux auteurs de définir les conditions nécessaires à l'obtention de microémulsions monophasiques incorporant de grandes quantités d'eau ou d'hydrocarbure. En appliquant la même méthode d'étude, Kunieda et Shinoda, (34–35), ont montré que le comportement de systèmes incorporant l'Aérosol OT comme unique amphiphile est globalement analogue à celui de systèmes à surfactants non-ioniques. Au cours de leurs travaux, Shinoda et ses collaborateurs ont accordé une attention toute particulière à l'effet de la température sur le comportement des systèmes à surfactants non-ioniques. Cela les a conduits, en règle générale, à considérer comme un paramètre la concentration du surfactant dans les systèmes et donc à déterminer l'organisation des diagrammes des phases des systèmes étudiés en fonction de deux variables, la température et la teneur relative en eau, (ou en hydrocarbure). Pour des raisons liées aux objectifs généraux de leurs travaux, Shinoda et ses collaborateurs ont essentiellement étudié des systèmes caractérisés par des valeurs de la concentration en surfactant de l'ordre de ou inférieures à 10 %, ce qui, d'un certaine façon, limite la portée générale des résultats obtenus par ces chercheurs. D'autres auteurs ont adopté une approche complémentaire en traitant la température comme un paramètre, ce qui les a conduits à déterminer, à température donnée, des diagrammes de phases en fonction des concentrations des trois constituants de base des systèmes, eau, hydrocarbure et surfactant non-ionique. A titre d'exemples, ou peut citer les travaux de Lo et al., (36), Hermann et al., (37–38), Mathis et al., (39),

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Boyle et al., (40), et Friberg et al., (41—42). Les résultats acquis par ces auteurs montrent que, dans le diagramme ternaire eau/surfactant/hydrocarbure, la configuration du domaine d'existence de milieux du genre microémulsion varie énormément en fonction de certains paramètres, tels que la nature de l'hydrocarbure ou la température. Les résultats obtenus par Mathis et al., (39), Boyle et al., (40), et Friberg et al., (41—42), montrent que, dans le diagramme tri-dimensionnel concentration-température des systèmes étudiés, le domaine d'existence de milieux du genre microémulsion est d'un seul tenant, ce qui permet de comprendre pourquoi, suivant la valeur de la température, le domaine de microémulsion déterminé dans le diagramme ternaire eau/surfactant/hydrocarbure peut être constitué soit d'une seule région, soit de deux ou trois régions disjointes. Nilsson et Lindman, (43), ont mis à profit cette constatation d'ordre expérimental pour tenter, par des expériences de résonance magnétique nucléaire, de déterminer la structure du milieu dans les différentes régions de microémulsion de trois systèmes eau lourde/surfactant/hydrocarbure analogues à ceux étudiés par Friberg et al., (41—42). Les résultats ainsi obtenus en ce qui concerne les variations, en fonction de la composition, des coefficients d'auto-diffusion de l'eau lourde, de l'hydrocarbure et du surfactant tendent à montrer que, sur la plus grande partie du domaine de microémulsion, il n'existe pas d'interfaces eau/hydrocarbure nettement structurés et que la formation de microémulsions au sens de Schulman, (2), c'est-à-dire de dispersions de micro-gouttelettes d'eau en milieu organique ou de micro-gouttelettes d'hydrocarbure en milieu aqueux, ne se produit que dans des régions correspondant à des compositions très riches en hydrocarbure ou très riches en eau. En ce qui concerne les systèmes incorporant des surfactants ioniques, il convient de rappeler en premier lieu les travaux de Ekwall et al., (1), qui constituent une référence, car ils forment un catalogue assez complet des différents types d'organisation interne des diagrammes des phases de systèmes comportant un corps organique, un surfactant ionique et l'eau. Les diagrammes publiés par ces auteurs montrent notamment que le domaine d'existence de milieux du genre microémulsion peut avoir une configuration très variée, qui est fonction de la nature du corps organique et de celle du surfactant ionique. Différents groupes d'auteurs ont consacré une partie de leurs travaux à la détermination des domaines de microémulsion de systèmes quaternaires classiques eau/surfactant ionique/alcool/hydrocarbure, considérée comme le point de départ d'études de la structure de ce type de microémulsions. Afin de mettre en évidence les relations existant entre microémulsions quaternaires et solutions monophasiques ternaires eau/surfactant ionique/alcool, Friberg et collaborateurs, (44—47), ont étudié de façon assez complète le système eau/oléate de potassium/hexanol-1/benzène, en associant diverses techniques à la méthode des diagrammes des phases. Ils ont pu ainsi montrer, d'une part, que le domaine d'existence de microémulsions du genre eau-dans-hydrocarbure du système considéré, (microémulsions «inverses»), constitue le développement en trois dimensions du domaine d'existence de solutions monophasiques eau-dans-alcool, (solutions micellaires «inverses» L_2), d'autre part, que microémulsions inverses et solutions micellaires inverses présentent des analogies de comportement en ce qui concerne l'évolution

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de certaines de leurs propriétés physico-chimiques avec la teneur en eau. Il apparaît en particulier que solutions micellaires inverses et microémulsion sont, pour des teneurs en eau faibles, des suspensions en milieu organique d'agrégats pré-micellaires, formés de molécules d'eau fortement liées à des molécules de surfactant, et ne contiennent de véritables microgouttelettes d'eau, possédant un coeur aqueux entouré d'un film interfacial de molécules de surfactant et d'alcool, que pour des teneurs en eau caractérisées par un rapport molaire eau/surfactant supérieur à 10 environ. De ces résultats, Friberg et al. ont tiré la conclusion qu'il y a continuité de structure entre solutions micellaires inverses et microémulsions inverses. D'autres auteurs ont également abouti à cette conclusion, (48). Les relations existant entre microémulsions quaternaires du genre hydrocarbure-dans-eau, (microémulsions «directes»), et solutions monophasiques alcool-dans-eau, (solutions micellaires «directes» L_1), ont été également étudiées par Friberg et collaborateurs, (49—53). Les résultats obtenus montrent que la formation et la stabilité des microémulsions directes sont des phénomènes complexes sur lesquels certains paramètres de composition tels que le rapport eau/surfactant et la nature de l'hydrocarbure ont une influence très marquée. Podzimek et Friberg, (51) ont trouvé que certaines microémulsions directes ne sont pas thermodynamiquement stables, ce qui est à rapprocher d'observations rapportées par d'autres auteurs, (54—57). Des diagrammes des phases publiés par Friberg et collaborateurs, (51—52), montrent que le domaine en trois dimensions correspondant à l'existence de microémulsions directes peut avoir une configuration tourmentée, ce qui explique la diversité de configuration

présentée par les régions de microémulsions directes dans des diagrammes pseudo-ternaires définissant des coupes du domaine tri-dimensionnel de microémulsion, en fonction de tel ou tel paramètre. Cela est à rapprocher d'observations concernant la configuration des domaines de microémulsion de certains systèmes à surfactants non-ioniques, (39—42). On peut d'ailleurs rappeler à ce propos que Shinoda et al., (58), ont montré qu'il existe des similarités entre diagrammes des phases de systèmes à surfactants non-ioniques et diagrammes des phases de systèmes à combinaisons d'un surfactant ionique et d'un cosurfactant. Un fait expérimental important qui ressort des résultats de Friberg et collaborateurs, (51—53), est que le domaine de microémulsions directes peut s'étendre jusqu'à des régions du diagramme des phases correspondant à des compositions dont l'hydrocarbure est le constituant nettement majoritaire. La possibilité, ainsi démontrée par des études de diagrammes des phases, de former des milieux «directs» à très forte teneur en hydrocarbure incite à entreprendre des recherches concernant leur nature exacte et les conditions nécessaires à leur formation et à leur stabilité, recherches dont les résultats pourraient être d'un grand intérêt, tant scientifique que technique. Des déterminations de domaines de microémulsion de systémes quaternaires eau/surfactant ionique/alcool/hydrocarbure ont été effectuées par Bellocq et al., (24, 59—64), qui s'en sont servi comme support d'études de structure utilisant des techniques variées, (viscosimétrie, électroconductimétrie, résonance et relaxation magnétique nucléaire, micrographie électronique, diffusion de la lumière, mesures de tension de vapeur). Les nombreuses

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données expérimentales ainsi acquises montrent que les microémulsions non-saturées présentent une grande diversité de structures et que les transitions structurales se produisent de façon progressive lorsque la composition du milieu varie. Il apparaît que, dans certaines régions du domaine de microémulsion, la structure du milieu peut être identifiée sans ambiguïté, (populations de microgouttelettes d'eau ou d'hydrocarbure, agrégats pré-micellaires). Par contre, il semble que, dans d'autres régions telles que la partie «centrale» du domaine de microémulsion, la structure du milieu soit mal définie, les données expérimentales tendant à indiquer que les interfaces eau/hydrocarbure sont peu structurés. Des constatations analogues ont été rapportées par d'autres auteurs, (65–70). Bellocq et al., (71–74), ont également déterminé l'organisation des diagrammes des phases de systèmes donnant naissance à des milieux polyphasiques variés possédant des phases du genre microémulsion. Des études du comportement de ces millieux polyphasiques et des propriétés de leurs phases du genre microémulsion ont été entreprises, qui ont montré l'existence de phénomènes de criticité.

Les travaux rappelés ci-dessus à titre d'exemples démontrent l'utilité et la fécondité des études de diagrammes des phases de systèmes à composés amphiphiles, surtout lorsqu'elles sont associées à des études visant à déterminer, grâce à des techniques variées, la structure et les propriétés physico-chimiques de différents types de milieux obtenus, qu'il s'agisse de méso-phases ou de phases du genre microémulsion. Des informations d'ordre général sur la structure des micro-émulsions monophasiques non-saturées ou de microémulsions appar-

tenant à des milieux polyphasiques peuvent être obtenues assez simplement en corrélant résultats d'études de diagrammes des phases et résultats d'études de propriétés de transport, (viscosité, conductivité électrique, coefficients de diffusion...). Cette méthode a été utilisée par Bennett et al., (75), pour étudier, dans le cas de systèmes à surfactants ioniques et alcools, les microémulsions constituées par les phases riches en surfactant de systèmes diphasiques et triphasiques du type Winsor, (22). Les résultats ainsi obtenus, en particulier ceux concernant la viscosité et la conductivité électrique, on conduit ces auteurs à conclure que, au cours de la transition Winsor I→Winsor III→Winsor II induite par l'augmentation de la salinité de la phase aqueuse, la microstructure de la phase riche en surfactant évolue de façon progressive. Pour les plus faibles et les plus fortes salinités, la phase riche en surfactant serait une microémulsion au sens de Schulman, (2), c'est-à-dire une population de micro-gouttelettes du type hydrocarbure-dans-eau, (faibles salinités), ou une population de micro-gouttelettes du type eau-dans-hydrocarbure, (fortes salinités). Pour les salinités intermédiaires, notamment celles qui induisent la formation d'un milieu triphasique du type Winsor, la phase riche en surfactant serait une mosaïque dynamique de micro-domaines aqueux et organiques séparés par des films interfaciaux très flexibles, situation qui a été modélisée par Scriven et d'autres auteurs, (76–80), sous le nom de «structure bicontinue». C'est aussi cette méthode qui a été appliquée par différents groupes d'auteurs à l'étude de microémulsions monophasiques non-saturées de systèmes à surfactants ioniques et alcools. Comme exemples d'études de phénomènes d'autodif-

fusion couplées à des études de diagrammes des phases, on peut citer les travaux, déjà mentionnés, de Lindman et al., (68–70), et ceux de Larche et al., (81), qui ont également étudié le phénomène de conduction électrique dans les microémulsions non-saturées. Sans avoir déterminé de façon explicite des diagrammes des phases, Shah et collaborateurs, (82–88), ont étudié, en fonction de la composition, la viscosité, la conductivité électrique et la permittivité de microémulsions monophasiques non-saturées, en vue d'obtenir des renseignements concernant leur structure. En complément à des études de la permittivité et de la conductivité électrique de microémulsions monophasiques non-saturées, Clausse et al., (89–101), ont procédé à la détermination des domaines de microémulsion de nombreux systèmes quaternaires eau/surfactant ionique/ alcool/hydrocarbure. Cela a permis à ces auteurs d'établir des corrélations entre configuration du domaine de microémulsion et comportement électroconductif des microémulsions, et de délimiter, à l'intérieur du domaine de microémulsion, des régions pouvant correspondre à différents types de structures. Les résultats publiés par Clausse et al., (89–101), relatifs à des systèmes eau/surfactant ionique/alcool paraffinique/hydrocarbure, incorporant divers surfactants, alcools et hydrocarbures mais caractérisés par une valeur donnée, de l'ordre de 1/2, du rapport massique surfactant/alcool, ont pu être généralisés grâce à une analyse détaillée de la configuration du domaine de microémulsion dans le tétraèdre des phases de quatre systèmes modèles eau/dodécylsulfate de sodium/alcool/n-dodécane, incorporant l'un ou l'autre des quatres alcools suivants: butanol-1, pentanol-1, hexanol-1 et heptanol-1, (102). En complément, des expériences de vis-

cosimétrie et d'électroconductimétrie ont été effectuées, qui visaient à permettre une identification de la structure des microémulsions dans différentes régions de leurs domaines d'existence. Cette étude, dont les résultats détaillés seront publiés dans de prochains articles, (103–106), a permis de montrer que la configuration générale du domaine tri-dimensionnel de microémulsion d'un système quaternaire eau/surfactant/alcool/hydrocarbure est conditionnée de façon essentielle par celle du domaine de solubilisation mutuelle de l'eau, du surfactant et de l'acool. Il apparaît en particulier que, dans le cas de systèmes incorporant un alcool long, (hexanol-1 ou heptanol-1, pour les systèmes considérés), la transition microémulsions directes ↔ microémulsions inverses, («inversion des phases»), se produit toujours par l'intermédiaire, soit de milieux polyphasiques à phases isotropes, (milieux du type «Winsor» (22)), soit de milieux mésomorphes ou comportant une phase mésomorphe, alors que, dans le cas de systèmes incorporant un alcool court, (butanol-1 ou pentanol-1, pour les systèmes considérés), l'inversion des phases peut se produire de façon diffuse, sans provoquer des discontinuités des propriétés macroscopiques du milieu, puisqu'il existe des chemins expérimentaux situés entièrement dans le domaine de microémulsion et reliant les régions des compositions riches en eau aux régions des compositions riches en hydrocarbure. L'existence de deux catégories de systèmes est confirmée de façon très nette par les résultats de l'étude des comportements rhéologique et électroconductif des microémulsions, sur lesquels, toutes choses égales par ailleurs, la longueur de la molécule d'alcool a une influence considérable. Dans le cas de systèmes incorporant un alcool

court, la conduction électrique dans les microémulsions semble résulter d'un phénomène de percolation, (107), la conductivité électrique croissant, tout d'abord très rapidement, suivant une loi d'échelle, puis linéairement, avec la teneur en eau. Ce phénomène n'existe pas dans le cas de systèmes incorporant un alcool long, la conductivité électrique sur la région d'existence des microémulsions inverses gardant des valeurs faibles, (de l'ordre de $5 \cdot 10^{-3}$ Sm^{-1}), et variant de façon non-monotone avec la teneur en eau. Une analyse de ce comportement électroconductif, qui peut s'expliquer à partir d'un modèle proposé par Eicke et Denss, (108), conduit à suggérer que le domaine des microémulsions inverses des systèmes à alcools longs comporterait une région d'existence d'agrégats pré-micellaires, (faibles teneurs en eau), et une région d'existence de véritables émulsions inverses, c'est-à-dire de microgouttelettes comportant un coeur aqueux délimité par un film de molécules de surfactant et d'alcool, et dispersées dans une phase essentiellement organique. Parallèlement, l'expérience montre que le comportement rhéologique des microémulsions incorporant un alcool court est très différent de celui des microémulsions incorporant un alcool long. L'ensemble de ces résultats, relatifs aux systèmes eau/dodécylsulfate de sodium/butanol-1, pentanol-1, hexanol-1, heptanol-1/n-dodécane, est cohérent avec des données expérimentales et théoriques concernant la structure des microémulsions et les interactions existant en leur sein, (12—21).

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